This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
New salicylaldimine nickel complexes, comprising only earth-abundant elements, have been developed for electrocatalytic hydrogen evolution in aqueous media. Second-sphere ether functionalities on the periphery of the complexes enhance the electrocatalytic activity in the presence of alkali metal cations. The electrocatalysts demonstrate improved performances especially in the economical and sustainable seawater reaction medium.

Global climate change has been widely attributed to the rampant consumption of fossil fuels and has stimulated recent efforts to develop alternative, more sustainable sources of fuels. An attractive solution is to develop artificial photosynthetic systems that can harvest sunlight, like a leaf, and store the solar energy in the form of chemical bonds in hydrogen (H₂) and oxygen (O₂) via water splitting. Energy storage is appealing since sunlight is intermittent. When alternative energy resources such as sunlight or geothermal energy can be efficiently converted into electricity, a critical challenge in creating a practical artificial photosynthetic system will be to develop commensurately efficient electrocatalysts for H₂ evolution from seawater.¹,¹⁴ Platinum (Pt) is a well-known electrocatalyst for the reduction of protons (H⁺) to H₂ in commercial electrolysers, with a low overpotential (η), long durability, and high turnover frequency (TOF).³ However, Pt is a precious metal, partly due to its relative scarcity in the Earth’s crust. Consequently, more earth-abundant, heterogeneous electrocatalysts have been sought and reported, including metal chalcogenides,⁵–⁷ carbides,⁸ phosphides,⁹–¹¹ and hydroxides,¹²,¹³ in attempts to produce H₂ at prices competitive with the production from fossil fuels. Concurrent with the research on heterogeneous catalysts, a number of molecular complexes consisting of earth-abundant elements have been found to be exceptional H₂ evolution electrocatalysts. These complexes display especially impressive TOFs in organic solvents, some of which surpass the activities of natural hydrogenase enzymes, and are supported by ligands including N₂P₂,¹⁴–¹⁷ macrocyclic oximes,¹⁸–²⁰ polypyridines,²¹,²² thiolates,²³–²⁶ and porphyrins.²⁷ A select few of the molecular electrocatalysts are active in aqueous media and ligated by scaffolds including PYSMe₂,²⁸ DPA-Bpy,²⁹ and P₄N₂.³⁰ Co salicylaldimine catalysts have also been used for photodriven H₂ evolution in water.³¹ Among the most active catalysts, a common feature has been the judicious customisation of the second coordination sphere via the introduction of bioinspired H⁺ relays. These complexes poise Lewis basic amine and Bronsted acidic alcohol groups in close proximity to the redox-active metal centre, similar to natural enzymatic systems. However, few studies have documented the effects of alkali metal ions in the second coordination sphere of molecular H₂ evolution electrocatalysts, although copious amounts of alkali metal cations are found in seawater and biological systems. Herein, we describe the H₂ evolution activity of new nickel (Ni) complexes supported by salicylaldimine ligands with pendant, chelating ether groups that can bind Lewis acids such as alkali metal cations. The alkali metal ion-binding capabilities of salen-type ligands without pendant ether functionalities have been previously observed in molecular CO₂ complexes.³² The role of alkali metal cations is important since they constitute the most practical and cheapest electrolytes, and will be especially relevant if seawater (Na⁺) is to become the ultimate aqueous medium for large-scale H⁺ reduction.

We demonstrate that our water-soluble Ni electrocatalysts, which are readily accessible in a few steps from commercially available chemicals (Scheme 1), behave as H₂ evolution catalysts under both neutral and acidic aqueous solutions.

---

¹ Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371.
² Singapore Berkeley Research Initiative for Sustainable Energy (SimBioRISE), 1 Create Way, Singapore 138602.
³ Solar Fuels Laboratory, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798.
⁴ Energy Research Institute@NTU (ERI@N), Nanyang Technological University, Research Techno Plaza, Singapore 637553.
⁵ # Current address: Department of Advanced Materials Science and Nanotechnology, University of Science and Technology of Hanoi (Vietnam France University), 18 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam

Electronic Supplementary Information (ESI) available: Detailed synthetic procedures and characterisation, additional electrochemistry data, XPS results, TEM, and DLS data are included. CCDC 1435734-1435735. For ESI and crystallographic data in CIF or other electronic formats, see DOI: 10.1039/c000000x/
Moreover, the chelating methoxethoxy can bind hydrated alkali metal cations to provide hydrogen-bonding stabilisation and enhanced electrocatalytic proton reduction reactivity.

The redox couple becomes increasingly reversible at scan rates up to 1.0 V s⁻¹, which may be due to structural reorganisation or precipitation of the triply anionic transient species on the electrode. In the presence of acetic acid (HOAc) as a weak proton donor in DMF, the CVs show moderate current increases with little change to the onset current (Figure S5), indicating that 6a behaves as an electrocatalyst for H₂ evolution even with weak acids. When the stronger trifluoroacetic acid (TFA) was used as the proton source, the CV displayed a dramatic increase in the catalytic current over the background (Figure 1a), with an anodic shift of the onset current. After varying the concentration of TFA added, the CVs reveal a 2nd order dependence on the acid concentration (Figure S6). Attempts to perform a foot-of-the-wave analysis on H₂ evolution in the presence of TFA have been complicated by significant deviations from linearity due to the anodic onset shift at higher TFA concentrations (Figure S7). This onset shift could be due to equilibrium protonation of the phenoxide donor at high acid concentrations (ESI), which reduces the overpotential required for electrocatalytic H₂ evolution by positioning protons in close proximity to the Ni centre. Instead, foot-of-the-wave analysis using acetic acid as the proton donor demonstrates the expected linear behaviour, yielding an apparent rate constant of 17.9 M⁻¹ s⁻¹ in 0.10 M acetic acid at a scan rate of 100 mV s⁻¹ (Figure S8).

Figure 1. CVs of (a) 1.0 mM of 6a in 0.10 M n-Bu₄NPF₆ in DMF with different concentrations of TFA; (b) 1.0 mM 6a in 0.10 M Na₂SO₄ with different HOAc concentrations at scan rates of 100 mV s⁻¹ with a glassy carbon working electrode (3 mm diameter).

Interestingly, the CV of 6a in neutral water with Na₂SO₄ as the electrolyte exhibits a remarkable increase in the catalytic current at an onset of ~1.05 V vs. NHE, corresponding to an overpotential of 0.59 V. Gas bubbles are also observed during cathodic scans. The overpotential of 6a is comparable to or lower than other molecular electrocatalysts that contain first-row transition metals and function in neutral water with glassy carbon working electrodes. For instance, the overpotentials for Co complexes ligated by P₂N₅ ligands or DPA-Bpy are about 0.55 and 0.78 V respectively, with glassy carbon working electrodes. When 0.10 M aqueous acetic acid is used (pH = 2.8), the catalytic onset shifts to ~0.64 V, which is larger than the expected Nerstian shift of about 0.24 V due to an increase in [H⁺] by about four orders of magnitude (Figure 1b). In addition, the catalytic current shows a 1st order dependence on the concentration of 6a (Figure 2a), suggesting that H₂ evolution occurs via protonation of a mononuclear Ni intermediate, rather than bimolecular coupling of two highly anionic Ni complexes (Scheme S1).

The cyclic voltammogram (CV, Figure S4) of 6a in N,N-dimethylformamide (DMF) features a quasi-reversible redox couple at ~1.04 V vs. NHE assigned to a metal-based Ni⁺/Ni⁰ redox couple. The redox wave becomes increasingly reversible at scan rates up to 1.0 V s⁻¹, which may be due to structural reorganisation or precipitation of the triply anionic transient species on the electrode. In the presence of acetic acid (HOAc) as a weak proton donor in DMF, the CVs show moderate current increases with little change to the onset current (Figure S5), indicating that 6a behaves as an electrocatalyst for H₂ evolution even with weak acids. When the stronger trifluoroacetic acid (TFA) was used as the proton source, the CV displayed a dramatic increase in the catalytic current over the background (Figure 1a), with an anodic shift of the onset current. After varying the concentration of TFA added, the CVs reveal a 2nd order dependence on the acid concentration (Figure S6). Attempts to perform a foot-of-the-wave analysis on H₂ evolution in the presence of TFA have been complicated by significant deviations from linearity due to the anodic onset shift at higher TFA concentrations (Figure S7). This onset shift could be due to equilibrium protonation of the phenoxide donor at high acid concentrations (ESI), which reduces the overpotential required for electrocatalytic H₂ evolution by positioning protons in close proximity to the Ni centre. Instead, foot-of-the-wave analysis using acetic acid as the proton donor demonstrates the expected linear behaviour, yielding an apparent rate constant of 17.9 M⁻¹ s⁻¹ in 0.10 M acetic acid at a scan rate of 100 mV s⁻¹ (Figure S8).

Interestingly, the CV of 6a in neutral water with Na₂SO₄ as the electrolyte exhibits a remarkable increase in the catalytic current at an onset of ~1.05 V vs. NHE, corresponding to an overpotential of 0.59 V. Gas bubbles are also observed during cathodic scans. The overpotential of 6a is comparable to or lower than other molecular electrocatalysts that contain first-row transition metals and function in neutral water with glassy carbon working electrodes. For instance, the overpotentials for Co complexes ligated by P₂N₅ ligands or DPA-Bpy are about 0.55 and 0.78 V respectively, with glassy carbon working electrodes. When 0.10 M aqueous acetic acid is used (pH = 2.8), the catalytic onset shifts to ~0.64 V, which is larger than the expected Nerstian shift of about 0.24 V due to an increase in [H⁺] by about four orders of magnitude (Figure 1b). In addition, the catalytic current shows a 1st order dependence on the concentration of 6a (Figure 2a), suggesting that H₂ evolution occurs via protonation of a mononuclear Ni intermediate, rather than bimolecular coupling of two highly anionic Ni complexes (Scheme S1).

The cyclic voltammogram (CV, Figure S4) of 6a in N,N-dimethylformamide (DMF) features a quasi-reversible redox couple at ~1.04 V vs. NHE assigned to a metal-based Ni⁺/Ni⁰ redox couple. The redox wave becomes increasingly reversible at scan rates up to 1.0 V s⁻¹, which may be due to structural reorganisation or precipitation of the triply anionic transient species on the electrode. In the presence of acetic acid (HOAc) as a weak proton donor in DMF, the CVs show moderate current increases with little change to the onset current (Figure S5), indicating that 6a behaves as an electrocatalyst for H₂ evolution even with weak acids. When the stronger trifluoroacetic acid (TFA) was used as the proton source, the CV displayed a dramatic increase in the catalytic current over the background (Figure 1a), with an anodic shift of the onset current. After varying the concentration of TFA added, the CVs reveal a 2nd order dependence on the acid concentration (Figure S6). Attempts to perform a foot-of-the-wave analysis on H₂ evolution in the presence of TFA have been complicated by significant deviations from linearity due to the anodic onset shift at higher TFA concentrations (Figure S7). This onset shift could be due to equilibrium protonation of the phenoxide donor at high acid concentrations (ESI), which reduces the overpotential required for electrocatalytic H₂ evolution by positioning protons in close proximity to the Ni centre. Instead, foot-of-the-wave analysis using acetic acid as the proton donor demonstrates the expected linear behaviour, yielding an apparent rate constant of 17.9 M⁻¹ s⁻¹ in 0.10 M acetic acid at a scan rate of 100 mV s⁻¹ (Figure S8).

Interestingly, the CV of 6a in neutral water with Na₂SO₄ as the electrolyte exhibits a remarkable increase in the catalytic current at an onset of ~1.05 V vs. NHE, corresponding to an overpotential of 0.59 V. Gas bubbles are also observed during cathodic scans. The overpotential of 6a is comparable to or lower than other molecular electrocatalysts that contain first-row transition metals and function in neutral water with glassy carbon working electrodes. For instance, the overpotentials for Co complexes ligated by P₂N₅ ligands or DPA-Bpy are about 0.55 and 0.78 V respectively, with glassy carbon working electrodes. When 0.10 M aqueous acetic acid is used (pH = 2.8), the catalytic onset shifts to ~0.64 V, which is larger than the expected Nerstian shift of about 0.24 V due to an increase in [H⁺] by about four orders of magnitude (Figure 1b). In addition, the catalytic current shows a 1st order dependence on the concentration of 6a (Figure 2a), suggesting that H₂ evolution occurs via protonation of a mononuclear Ni intermediate, rather than bimolecular coupling of two highly anionic Ni complexes (Scheme S1).
To explore the effects of the pendant ether on 6a, CVs have been conducted in the presence of n-BuNCl, Li$_2$SO$_4$, Na$_2$SO$_4$, and KPF$_6$ as the electrolytes in 0.10 M acetic acid (Figure 2b). With n-BuN$^+$ as the electrolyte, the current density increases 0.70 mA cm$^{-2}$ above the background current at an overpotential of 0.84 V in electrolyte solution with no added acids (Figure S9). This indicates an appreciable, but slow H$_2$ evolution reaction. The n-BuN$^+$ cation is bulky and may hinder access to the Ni catalytic centre by hydronium ions, similar to the proton-gated hangman iron porphyrins reported by Nocera et al.\textsuperscript{43} In contrast, with Na$_2$SO$_4$ as the electrolyte, the current density is 8.2 times compared to the catalytic current with n-BuN$^+$ as electrolyte (Figure S9). We observe the highest electrocatalytic current with Li$^+$ as the electrolyte (11 times compared to n-BuN$^+$ as electrolyte, Figure S9) among the common and affordable cations examined. This dramatic increase in catalytic current highlights the non-innocence of the electrolyte in our H$_2$ evolution system, and emphasises the need for prudent management of second sphere effects around the catalytic centre (Scheme S1).	extsuperscript{44,46} In 0.10 M acetic acid, the electrocatalytic current increase also followed the same trend (Figure S10). The most Lewis acidic Li$^+$ corresponds to the fastest catalytic behaviour. The Li$^+$ with the highest charge density could more effectively introduce rigidity to the ether arms and direct H$^+$ to the Ni centre, or electrostatically reduce the overpotential via inductive effects. Since seawater contains copious amounts of Na$^+$ ions, judicious selection of pendant chelating groups that (size)-select for Na$^+$ may prove fruitful in improving the catalytic performance of 6a and are being explored.

In order to probe whether a heterogeneous catalyst is the major contributor of the H$_2$ evolution electrocatalysis, a series of standard electrochemical and spectroscopic experiments have been performed. The UV-vis, high-resolution mass, and $^1$H NMR spectra (Figure S11-13) before and after controlled potential electrolysis (CPE) indicate that 6a remains intact in solution, although there may be some adsorption. There were no nanoparticles observed by dynamic light scattering (DLS) measurements in the electrolyte solution after CPE for 2.5 h (Figure S14). The UV-vis spectra in Figure S10 show that the concentration of 6a decreased to 90% and 78% after 1 h and 2.5 h, respectively.\textsuperscript{1} We suspected that part of 6a was adsorbed on the carbon paper during the electrolysis process. To verify this conjecture, the used carbon paper electrodes in a CPE measurement were rinsed thoroughly with water before being subjected to CPE again (Figure S15). The used electrode showed a small, but non-negligible amount of catalytic activity. X-ray photoelectron spectroscopy (XPS) experiments were conducted on 6a and the used carbon paper electrode after CPE (Figures S16-17). The data indicate that the small amounts of deposited material on the electrode have almost identical composition as 6a, based on the XPS energies (Figure S16 and Table S11). We propose that some of the highly anionic 6a is deposited on the carbon paper electrode upon reduction during catalysis, and cannot be readily rinsed off. A transmission electron microscopy (TEM) image (Figure S18) of the solution after CPE also exhibits little evidence of nanoparticle formation. Majority of the H$_2$ evolution electrocatalysis is still attributed to 6a in homogeneous solution instead of deposited or suspended nanoparticles.

Controlled potential electrolysis (CPE) experiments with a mercury pool electrode have been conducted to confirm the identity of the product by gas chromatography and gauge the stability of 6a under catalytic conditions. The CPE measurements were performed in seawater obtained off the coast of Singapore (details in the ESI) with a mercury pool working electrode and a carbon rod counter electrode, at an overpotential of 0.84 V. As shown in Figure 3a, the amount of H$_2$ produced increased dramatically with a TON of 6.6 mol H$_2$ mol$^{-1}$ catalyst cm$^{-2}$ after 2 h, suggesting that 6a is indeed suitable as a H$_2$ evolution catalyst with seawater as the medium. However, the Faradaic efficiency of H$_2$ production in seawater is only around 82%, since we have a one-compartment cell and some of the O$_2$ produced at the anode will be reduced at the cathode (Figure S19). To explore the effect of the cations in the electrolyte, CPE was also conducted with n-BuN$_2$Cl, Li$_2$SO$_4$, Na$_2$SO$_4$, KPF$_6$, and MgSO$_4$ as the electrolytes in 0.10 M acetic acid solutions (Figure 3b). The TON with KPF$_6$ as the electrolyte was the highest in these experiments (Table S12). We propose that the poor solubility of our Li and Mg complexes led to catalyst precipitation and amalgamation into the mercury pool electrode during CPE, which resulted in a discrepancy with the CV and CPE data that we collected using carbon-based electrodes. Nonetheless,
these CPE measurements and the TON and TOF (Table S12) confirm that 6a remains active for electrocatalytic H⁺ reduction under almost neutral, saline aqueous conditions containing Na⁺ or K⁺, even when mercury electrodes are used to suppress the activity of nanomaterials.

Conclusions

We have prepared new mononuclear Ni complexes with salicyldimine ligands that can be used as electrocatalysts for the production of H₂ in both neutral and acidic aqueous solutions. The chelating ether groups in the structure can bind alkali metal cations to form Lewis acids and promote the H⁺ reduction efficiency. Future studies will focus on modification of the Ni complexes with electron withdrawing substituents to reduce the overpotential, applying 6a in photocatalytic units for H₂ evolution, and grafting the molecules on semiconductors for artificial photosynthesis.47, 48

HSS is supported by a NTU start-up grant (M4081012), the Nanyang Assistant Professorship (M4081154), and an MOE Tier 1 grant (M4011154). The authors acknowledge the funding support from the Singapore-Berkeley Research Initiative for Sustainable Energy (SinBerISE) CREATE Programme. The authors also thank Asst. Prof. Jason Xu Zhichuan from the NTU Solar Fuels Laboratory for support in electrochemistry and both Dr. Li Yongxin and Dr. Rakesh Ganguly for solving and refining the crystal structures in the ESI.

Notes and references

† The onset overpotential is defined as the difference between the reversible potential of the H⁺/H₂ redox couple of neutral DI water (-0.46 V vs. NHE at pH 7.6) and the potential at which 10% of the current value at the peak potential was reached.
† The charge during CPE were 38 and 94 C at 1 and 2.5 h respectively, in excess of the charge needed to reduce Ni²⁺ to Ni⁰ (0.12 and 0.26 C for 10% and 22% 6a respectively).